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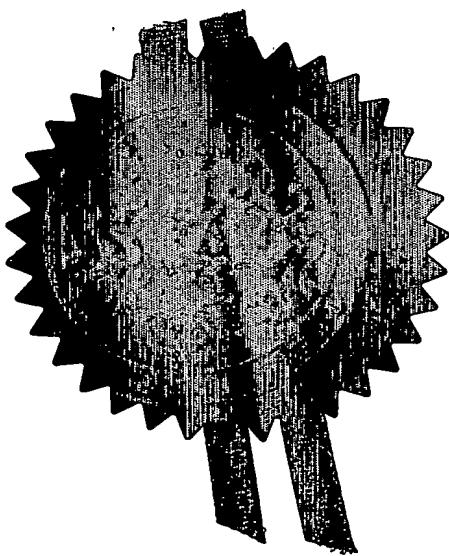
PCT

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Signed *Stephen Hordley*  
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# Patents Form 1/77

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## Request for grant of a patent

1. Your Reference **APB/GRK/Y700** **0306333.6**

**20 MAR 2003**

2. Application number

3. Full name, address and postcode  
of the or each Applicant

**Advanced Gel Technology Limited**  
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Country/state of incorporation  
(if applicable)

**7352999001**

Incorporated in: United Kingdom

4. Title of the invention **RESTRICTING FLUID PASSAGE AND NOVEL  
MATERIALS THEREFOR**

5. Name of agent **APPLEYARD LEES**

Address for service in the UK to  
which all correspondence should  
be sent  
**15 CLARE ROAD**  
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Patents ADP number **190001**

6. Priority claimed to: Country Application number Date of filing

7. Divisional status claimed from: Number of parent application Date of filing

8. Is a statement of inventorship and  
of right to grant a patent required in  
support of this application? **YES**

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9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form

Description 27

Claim(s)

Abstract

Drawing(s)



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10. If you are also filing any of the following, state how many against each item

Priority documents

Translation of priority documents

Statement of inventorship and right to grant a patent (PF 7/77)

Request for a preliminary examination and search (PF 9/77)

Request for substantive examination (PF 10/77)

Any other documents (please specify)

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11.

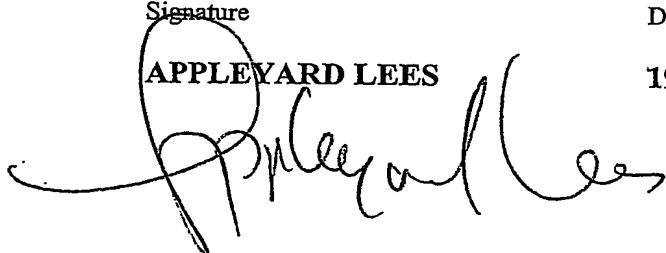
We request the grant of a patent on the basis of this application.

Signature

Date

APPLEYARD LEES

19 March 2003.



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12. Contact

- 01422 330110

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**RESTRICTING FLUID PASSAGE AND NOVEL MATERIALS THEREFOR**

This invention relates to the restriction of fluid passage and novel materials therefore. Particularly, although not 5 exclusively, the invention relates to a method of reducing the production of water from a water and oil or gas producing subterranean formation.

Fluid communication in the near well bore between a 10 hydrocarbon production interval or a drive fluid injection interval and an underlying aquifer can diminish hydrocarbon recovery from the associated hydrocarbon-bearing formation. Fluid communication can occur either across permeable matrix separating the interval from the 15 aquifer or via one or more vertical fractures or a fracture network connecting the interval and the aquifer.

When hydrocarbons are produced from a formation across a near well bore production interval into the well bore 20 penetrating the formation, water from an underlying aquifer tends to migrate upward into the production interval if there is fluid communication between the interval and the aquifer. Migration of water into the production interval is termed water coning. There are two 25 negative consequences of water coning. The first is that water residing in the production interval can block or significantly diminish the flow of hydrocarbons from the outlying formation into the well bore. The second consequence is that water production can compete with and 30 diminish hydrocarbon production. As a result, the ratio of water to hydrocarbons produced from the well bore can become unacceptably high when water coning occurs.

Water coning is extremely difficult to remedy whether fluid communication between the interval and aquifer is across vertical fractures or matrix. A traditional method of treating water coning is to cement the well bore over 5 the lower portion of the production interval. Unfortunately, well bore cementing at best only slightly reduces water coning and subsequent water production. Water coning usually recurs at the uncemented upper portion of the production interval shortly after the 10 cement treatment, negating the effectiveness of the treatment.

Another means of treating water coning is to inject gels into the fractures or matrix providing fluid communication 15 with the production interval. A gel treatment can block migration of aquifer water into the production interval but known treatments may also unacceptably damage the production interval because of the presence of gel in the interval. Known gels may be selectively placed in a 20 process referred to as "mechanical zone isolation" but disadvantageously such known gels tend to migrate into the production interval.

Water coning may be caused by poor vertical and areal 25 conformance in a hydrocarbon-bearing formation. "Vertical conformance" is a measure of the degree of geologic uniformity in permeability on moving across a hydrocarbon-bearing formation. "Areal conformance" is a measure of the degree of geologic uniformity in permeability on 30 moving horizontally across the formation.

Poor vertical conformance results from the vertical juxtaposition of relatively high permeability geologic

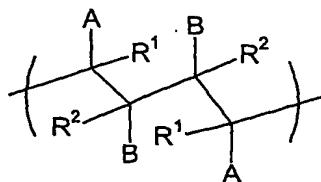
zones to relatively low permeability zones within a subterranean formation. Poor areal conformance results from the presence of high permeability streaks and high permeability anomalies within the formation matrix, such as vertical fractures and networks of the same, which have very high permeability relative to the formation matrix. Fluids generally exhibit poor flow profiles and sweep efficiencies in subterranean formations having poor vertical or areal conformance. Poor conformance is particularly a problem where vertical heterogeneity and/or fracture networks or other structural anomalies are in fluid communication with a subterranean wellbore across which fluids are injected or produced.

It is an object of the present invention to address the above described problems and other problems associated with restricting fluid passage.

According to a first aspect of the invention, there is provided a method of restricting passage of a fluid from a first location to a second location, the method comprising:

(a)

(i) selecting a first polymeric material having a repeat unit of formula

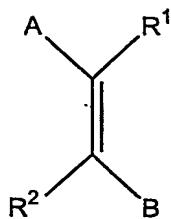


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wherein A and B are the same or different, are selected from optionally-substituted aromatic and heteroaromatic groups and at least one comprises a relatively polar atom or group and R<sup>1</sup> and R<sup>2</sup> independently comprise relatively 5 non-polar atoms or groups; or

(ii) selecting a first polymeric material prepared or preparable by providing a compound of general formula

10



wherein A, B, R<sup>1</sup> and R<sup>2</sup> are as described above, in an aqueous solvent and causing the groups C=C in said 15 compound to react with one another to form said first polymeric material;

(b) selecting a second polymeric material which includes a functional group which is able to react in the 20 presence of said first polymeric material to form a third polymeric material;

(c) causing the formation of said third polymeric material by a reaction involving said first and second 25 polymeric materials; and

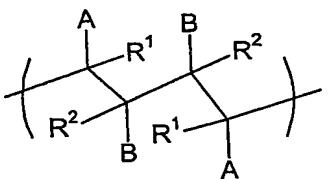
(d) arranging said third polymeric material between said first and second locations.

According to a second aspect of the invention, there is provided a method of restricting passage of a fluid from a first location to a second location, the method comprising positioning a polymeric material (herein "said third polymeric material") between said first and second locations, wherein said third polymeric material is a product of a reaction involving:

5

(a)

10 (i) a first polymeric material having a repeat unit of formula

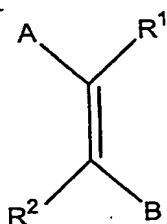


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15 wherein A and B are the same or different, are selected from optionally-substituted aromatic and heteroaromatic groups and at least one comprises a relatively polar atom or group and R<sup>1</sup> and R<sup>2</sup> independently comprise relatively non-polar atoms or groups; or

20

(ii) a first polymeric material prepared or preparable by providing a compound of general formula



25

wherein A, B, R<sup>1</sup> and R<sup>2</sup> are as described above, in an aqueous solvent and causing the groups C=C in said 5 compound to react with one another to form said first polymeric material; and

(b) a second polymeric material which includes a functional group which is able to react in the presence of 10 said first polymeric material to form said third polymeric material.

Whilst the methods of the first and second aspects may be used in any situation wherein it is desired to restrict 15 the passage of a fluid between first and second locations, the methods preferably comprise restricting the passage of a fluid, for example water (e.g. sea water) between two subterranean locations. Thus, there may be provided a method of reducing the production of water from a water 20 and oil producing subterranean formation which comprises contacting the formation with:

(a) a restrictor formulation which comprises a first polymeric material and a second polymeric material as 25 described above; and/or

(b) a third polymeric material as described above.

The invention extends to a method of plugging at least one 30 relatively high permeability region bounded by at least one relatively low permeability region in a hydrocarbon-bearing subterranean formation, said formation being penetrated by a well bore in fluid communication with said

at least one relatively high permeability region, the method comprising contacting said at least one relatively high permeability region with a restrictor formulation and/or a third polymeric material as described above.

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The methods described above preferably include injecting a said restrictor formulation into a subterranean formation and causing it to move to a desired location in which it may restrict passage of fluid (e.g. water) from a first 10 location to a second location (e.g. it may restrict passage of water through a relatively high permeability region of the formation). In said desired location the viscosity of the restrictor formulation preferably increases (compared to its viscosity when injected into 15 the formation) as it gels and forms said third polymeric material. The viscosity of the restrictor formulation immediately prior to injection into said subterranean formation may be less than 20cp, preferably less than 10cp, more preferably less than 8cp, especially less than 20 6cp. A relatively low viscosity enables the restrictor formulation to flow relatively easily through injection apparatus and into the formation. The viscosity of the restrictor formulation preferably increases over time until it forms a gel in said desired location. Suitably, 25 the formulation is such that it takes over 1 hour, preferably over 2 hours, more preferably over 3 hours, (measured from its preparation) at 25°C to form a solid gel (the viscosity of which remains substantially unchanged over time). This allows operators time to 30 inject the restrictor formulation and cause it to move to a desired location before its viscosity is too high. Advantageously, said restrictor formulation which is injected is inherently capable of gelling and the method

suitably does not require the restrictor formulation to contact another reactant (either injected into the subterranean formation separately or already present therein) to enable it to gel. Preferably, when the gel

5 has been formed in said desired location it is substantially immovably arranged therein so that it may set as a plug for a reasonable period of time such that it may improve water conformance and/or reduce water coning.

10 Said restrictor formulation preferably has a density at 25°C which is less than the density of pure water and preferably less than the density of sea water. Said restrictor formulation preferably has a density at 25°C of less than  $1.2 \text{ gcm}^{-3}$ . Advantageously, in view of its

15 density, the restrictor formulation may tend to migrate to a water-oil interface which may facilitate relatively accurate positioning of the restrictor formulation and, therefore, improve its effectiveness.

20 The ratio of the wt% of said first polymeric material to the wt% of said second polymeric material in said restrictor formulation is suitably less than 0.15, preferably less than 0.12, more preferably 0.1 or less. Said ratio may be at least 0.02, preferably at least 0.04,

25 more preferably at least 0.06, especially at least 0.07.

The sum of the wt% of the first and second polymeric materials in said restrictor formulation may be at least 2 wt%, preferably at least 3 wt%, more preferably at least 4

30 wt%. The sum may be less than 15 wt%, preferably less than 10 wt%, more preferably less than 8 wt%, especially less than 6 wt%.

Suitably, the amounts of "first polymeric material" and "second polymeric material" described refer to the sum of the amounts of first polymeric materials (if more than one type is provided) and the sum of the amounts of second 5 polymeric materials (if more than one type is provided).

Said restrictor formulation preferably includes water. In general terms water for use as described herein may be derived from any convenient source. It may be potable 10 water, surface water, sea water, aquifer water, deionised production water and filtered water derived from any of the aforementioned sources. The water may be treated so that it is suitable for use in the method. For example, it may be treated by addition of oxygen scavengers, 15 biocides, corrosion inhibitors, scale inhibitors, anti-foaming agents and flow improvers. Sea water and/or water from other sources may be deoxygenated and/or desulphonated. Said restrictor formulation may include at least 40 wt%, preferably at least 60 wt%, more preferably 20 at least 70 wt%, especially at least 85 wt% water. The amount of water is preferably less than 90 wt%.

Said restrictor formulation preferably further includes an additional component. Said additional component is 25 preferably substantially immiscible with pure water at 25°C. It is preferably organic. It is preferably non-polar. It is preferably less dense than water at 25°C. It may have a boiling point of greater than 110°C. It may be a hydrocarbon or an oil. Preferred hydrocarbons 30 include alkanes, preferably mixtures thereof such as diesel oil and kerosene. A said oil may be a vegetable oil. Said additional component is preferably provided as an emulsion in said restrictor formulation.

Said restrictor formulation may include 50 wt% or less, preferably 40 wt% or less, more preferably 30 wt% or less, especially 20 wt% or less of said additional component.

5 Said restrictor formulation may include 0 to 20 wt%, preferably 1 to 20 wt%, more preferably 2 to 15 wt%, especially 4 to 10 wt% of said additional component, especially an alkane containing material, such as diesel oil.

10

Said restrictor formulation preferably includes a catalyst for catalysing the reaction of the first and second polymeric materials. Said catalyst is preferably a protic acid. Said acid preferably has an acid dissociation 15 constant value of greater than  $10^{-6}$ , more preferably greater than  $10^{-4}$  and, especially, greater than  $10^{-2}$ . Said restrictor formulation suitably includes less than 5 wt%, preferably less than 2wt%, more preferably less than 1 wt%, especially less than 0.5 wt% of catalyst.

20

The pH of the restrictor formulation, suitably measured immediately prior to it being injected into a subterranean formation, is suitably less than 6, preferably less than 4, more preferably less than 2. The pH is suitably 25 greater than 1. The aforementioned protic acid included as a catalyst may be used to adjust the pH to the desired level.

30 Preferably, in the method, said restrictor formulation suitably comprising said first and second polymeric materials and, optionally, said additional component (e.g. diesel oil) and a said catalyst, is prepared at the surface and then injected into the subterranean formation.

Said formulation may be prepared by mixing said first and second polymeric materials together in water. Then, the additional component may be added and emulsified. Finally, the catalyst may be added to the formulation.

5.

In the materials described above, A and/or B could be multi-cyclic aromatic or heteroaromatic groups. Preferably, A and B are independently selected from optionally-substituted five or more preferably six-membered aromatic and heteroaromatic groups. Preferred heteroatoms of said heteroaromatic groups include nitrogen, oxygen and sulphur atoms of which oxygen and especially nitrogen, are preferred. Preferred heteroaromatic groups include only one heteroatom. 10 Preferably, a or said heteroatom is positioned furthest away from the position of attachment of the heteroaromatic group to the polymer backbone. For example, where the heteroaromatic group comprises a six-membered ring, the heteroatom is preferably provided at the 4-position relative to the position of the bond of the ring with the 15 polymeric backbone.

20 Preferably, A and B represent different groups. Preferably, one of A or B represents an optionally-substituted aromatic group and the other one represents an optionally-substituted heteroaromatic group. Preferably A represents an optionally-substituted aromatic group and B represents an optionally-substituted heteroaromatic group especially one including a nitrogen heteroatom such as a 25 pyridinyl group.

30 Unless otherwise stated, optionally-substituted groups described herein, for example groups A and B, may be

substituted by halogen atoms, and optionally substituted alkyl, acyl, acetal, hemiacetal, acetalalkyloxy, hemiacetalalkyloxy, nitro, cyano, alkoxy, hydroxy, amino, alkylamino, sulphinyl, alkylsulphinyl, sulphonyl, 5 alkylsulphonyl, sulphonate, amido, alkylamido, alkylcarbonyl, alkoxy carbonyl, halocarbonyl and haloalkyl groups. Preferably, up to 3, more preferably up to 1 optional substituents may be provided on an optionally substituted group.

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Unless otherwise stated, an alkyl group may have up to 10, preferably up to 6, more preferably up to 4 carbon atoms, with methyl and ethyl groups being especially preferred.

15

Preferably, A and B each represent polar atoms or group - that is, there is preferably some charge separation in groups A and B and/or groups A and B do not include carbon and hydrogen atoms only.

20

Preferably, at least one of A or B includes a functional group which can undergo a condensation reaction, for example on reaction with said second polymeric material. Preferably, A includes a said functional group which can undergo a condensation reaction.

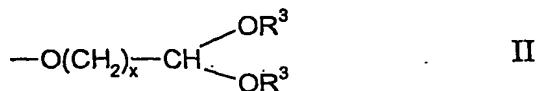
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Preferably, one of groups A and B includes an optional substituent which includes a carbonyl or acetal group with a formyl group being especially preferred. The other one of groups A and B may include an optional substituent which 30 is an alkyl group, with an optionally substituted, preferably unsubstituted, C<sub>1-4</sub> alkyl group, for example a methyl group, being especially preferred.

Preferably, A represents a group, for example an aromatic group, especially a phenyl group, substituted (preferably at the 4-position relative to polymeric backbone when A

35

represents an optionally-substituted phenyl group) by a formyl group or a group of general formula

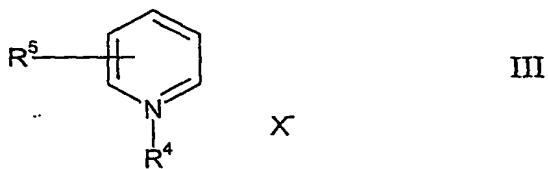


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where  $x$  is an integer from 1 to 6 and each  $\text{R}^3$  is independently an alkyl or phenyl group or together form an alkalene group.

10

Preferably,  $\text{B}$  represents an optionally-substituted heteroaromatic group, especially a nitrogen-containing heteroaromatic group, substituted on the heteroatom with a hydrogen atom or an alkyl or aralkyl group. More 15 preferably,  $\text{B}$  represents a group of general formula



20

wherein  $\text{R}^4$  represents a hydrogen atom or an alkyl or aralkyl group,  $\text{R}^5$  represents a hydrogen atom or an alkyl group and  $\text{X}^-$  represents a strongly acidic ion.

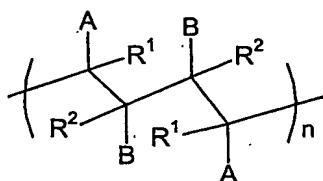
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Preferably,  $\text{R}^1$  and  $\text{R}^2$  are independently selected from a hydrogen atom or an optionally-substituted, preferably unsubstituted, alkyl group. Preferably,  $\text{R}^1$  and  $\text{R}^2$  represent the same atom or group. Preferably,  $\text{R}^1$  and  $\text{R}^2$  represent a hydrogen atom.

Preferred first polymeric materials may be prepared from any of the compounds described on page 3 line 8 to line 39 of GB2030575B by the method described in WO98/12239 and the 5 contents of the aforementioned documents are incorporated herein by reference.

Said first polymeric material may be of formula

10



15

wherein A, B, R<sup>1</sup> and R<sup>2</sup> are as described above and n is an integer. Integer n is suitably 10 or less, preferably 8 or less, more preferably 6 or less, especially 5 or less. Integer n is suitably at least 1, preferably at least 2, 20 more preferably at least 3. Preferably, formation of said third polymeric material from said first and second polymeric materials involves a condensation reaction. Preferably, formation of said third polymeric material involves an acid catalysed reaction. Preferably, said 25 first and second polymeric materials include functional groups which are arranged to react, for example to undergo a condensation reaction, thereby to form said third polymeric material. Preferably, said first and second polymeric materials include functional groups which are 30 arranged to react for example to undergo an acid catalysed reaction thereby to form said third polymeric material.

Preferably, said second polymeric material includes a functional group selected from an alcohol, carboxylic acid, carboxylic acid derivative, for example an ester, and an amine group. Said second polymeric material preferably includes a backbone comprising, preferably consisting essentially of carbon atoms. The backbone is preferably saturated. Pendent from the backbone are one or more said functional groups described. Said polymer may have a number average molecular weight ( $M_n$ ) of at least 10,000, preferably at least 50,000, especially at least 75,000.  $M_n$  may be less than 500,000, preferably less than 400,000. Said second polymeric material is preferably a polyvinyl polymer. Preferred second polymeric compounds include optionally substituted, preferably unsubstituted, polyvinylalcohol, polyvinylacetate, polyalkylene glycols, for example polypropylene glycol, and collagen (and any component thereof) and of these polyvinylalcohol and/or polyvinylacetate based polymeric materials are preferred.

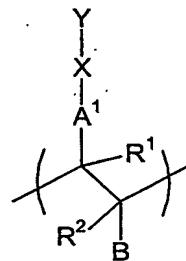
20 Said third polymeric material may be prepared from two different types of second polymeric materials suitably selected from those described above.

Where two types of second polymeric materials are used, preferably both are polyvinyl polymers and more preferably both are polyvinylalcohol polymers. The two types may have different number average molecular weight. One of the polymers may have a number average molecular weight which is at least 1.5, preferably at least 2, more preferably at least 2.5 times the molecular weight of the other.

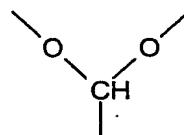
30 Preferably, said second polymeric material includes at least one vinyl alcohol/vinyl acetate copolymer which suitably includes greater than 50%, preferably greater than 65%, more preferably greater than 80wt% of vinyl alcohol moieties. Where two types of second polymeric material are provided both may be vinyl alcohol/vinyl acetate copolymers

of the type described. Preferably, said copolymers are substantially identical except for differences in their number average molecular weights. The provision of two types of second polymeric materials of different properties 5 (e.g. number average molecular weight) provides a means whereby the viscosity of a formulation of the first and second materials before reaction to form the third polymeric material may be adjusted.

10 Said third polymeric material suitably includes a moiety of formula



wherein R¹, R² and B are as described above, A¹ represents 15 a residue of group A described above after the reaction involving said first and second polymeric materials, Y represents a residue of said second polymeric material after said reaction involving said first and second polymeric materials and X represents a linking atom or 20 group extending between the residues of said first and second polymeric materials. In one preferred embodiment A¹ represents an optionally-substituted phenyl group, X represents a group



which is bonded via the oxygen atoms to a residue of said second polymeric material. For example, group X may be bonded to the polymer backbone of said second polymeric material.

5 According to a third aspect of the invention, there is provided a subterranean formation comprising a region having relatively poor natural water conformance and/or relatively high natural water coning, wherein said region 10 is plugged with a third polymeric material as described herein.

By "natural" we mean prior to human intervention with means directed at addressing poor conformance or water 15 coning problems.

It is believed that certain examples of restrictor formulations described herein are novel. Accordingly, in a fourth aspect, there is provided a restrictor 20 formulation comprising:

- (a) a first polymeric material as described herein;
- (b) a second polymeric material as described herein; and
- (c) an additional component as described herein.

25 Preferably, said restrictor formulation includes less than 40 wt%, more preferably less than 30 wt%, especially less than 20 wt% of said additional component. Said additional component preferably comprises a hydrocarbon and may be 30 diesel oil.

The invention extends to a receptacle containing at least 10 litres, preferably at least 100 litres, of a restrictor formulation as described herein.

- 5 Any feature of any aspect of any invention or embodiment described herein may be combined with any feature of any aspect of any other invention or embodiment described herein mutatis mutandis.
- 10 Specific embodiments of the invention will now be described, by way of example.

The following terms are used hereinafter:

- 15 "pbw" - means "parts by weight"  
diesel fuel - this refers to diesel fuel in the absence of surfactant additives present in commercial diesel.

- 20 In general terms, water conformance may be improved and/or water coning reduced in a subterranean hydrocarbon-bearing formation by forming a gel in or adjacent to a high permeability zone of a subterranean formation wherein it is desired to reduce permeability of the formation and therefore restrict the passage of water.

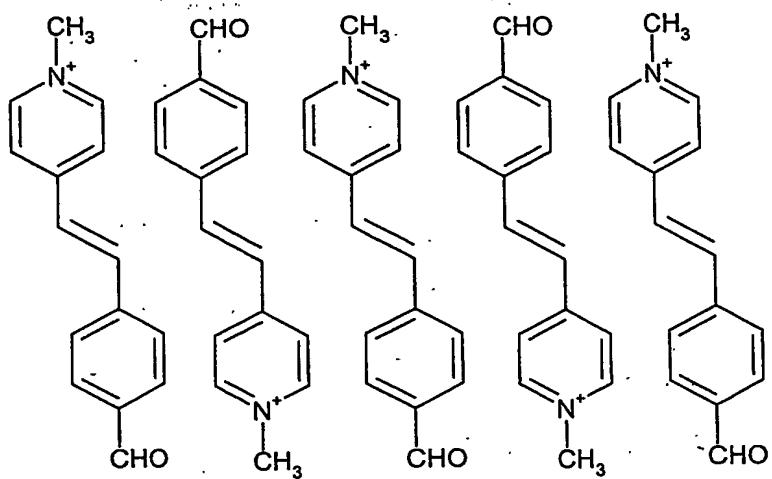
- 25 The gel is formed from a gel precursor formulation which comprises an aqueous formulation of poly (1,4-di(4-(N-methylpyridinyl))-2,3-di(4-(1-formylphenyl) butylidene), poly (vinyl alcohol), clean diesel fuel or kerosene in the presence of an acid catalyst. The gel precursor formulation may be prepared on the surface. The amounts/identity of the components may be varied to vary the time for the formulation to gel. The formulation is

initially of relatively low viscosity (2-5cp). It can readily be injected into a desired location within a subterranean formation. During its passage into the subterranean formation and subsequent thereto the precursor formulation gels as the butylidene polymer and the poly(vinyl alcohol) react. The gel, once formed, reduces the permeability of the formation and may therefore improve water conformance and/or reduce water coning.

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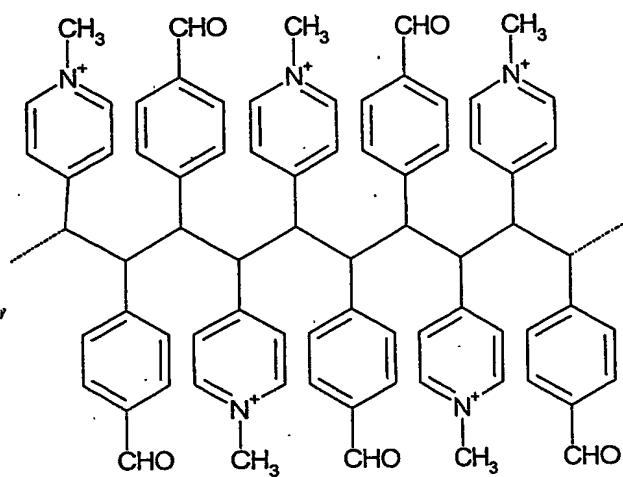
Example 1 - Preparation of poly (1,4-di(4-(N-methylpyridinyl))-2,3-di(4-(1-formylphenyl)butylidene

This was prepared as described in Example 1 of PCT/GB97/02529, the contents of which are incorporated herein by reference. In the method, an aqueous solution of greater than 1 wt% of 4-(4-formylphenylethenyl)-1-methylpyridinium methosulphonate (SbQ) is prepared by mixing the SbQ with water at ambient temperature. Under such conditions, the SbQ molecules form aggregates. The solution was then exposed to ultraviolet light. This results in a photochemical reaction between the carbon-carbon double bonds of adjacent 4-(4-formylphenylethenyl)-1-methylpyridinium methosulphate molecules (I) in the aggregate, producing a polymer, poly (1,4-di(4-(N-methylpyridinyl))-2,3-di(4-(1-formylphenyl)butylidene methosulphonate (II), as shown in the reaction scheme below. It should be appreciated that the anions of compounds I and II have been omitted in the interests of clarity.



I

>1% w/w Aqueous solution  
UV irradiation



II

Example 2

A formulation for use in reducing water conformance was prepared as follows:

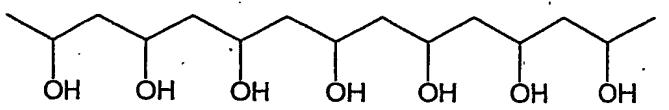
Water (95.5 pbw) at ambient temperature (about 25°C) was stirred at a low rate (to prevent foaming) and a

vinylalcohol/vinylacetate copolymer (containing 88% alcohol and 12% acetate units) (4.5 pbw) and the butylidene polymer of Example 1 (0.4 pbw) were added and stirring continued without a pause. After dissolution of copolymer and the 5 butylidene polymer, diesel fuel (10 pbw) was added with continuous stirring so that it became emulsified. Then, paratoluene sulphonic acid was added and thoroughly mixed into the formulation. This formulation had a viscosity of 2-5 cp.

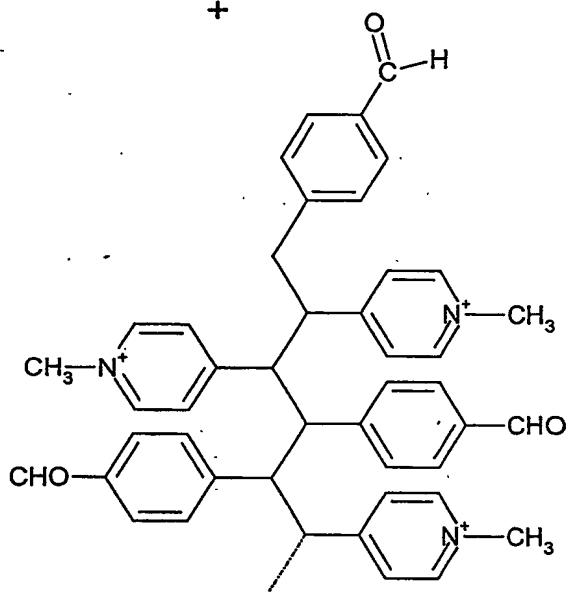
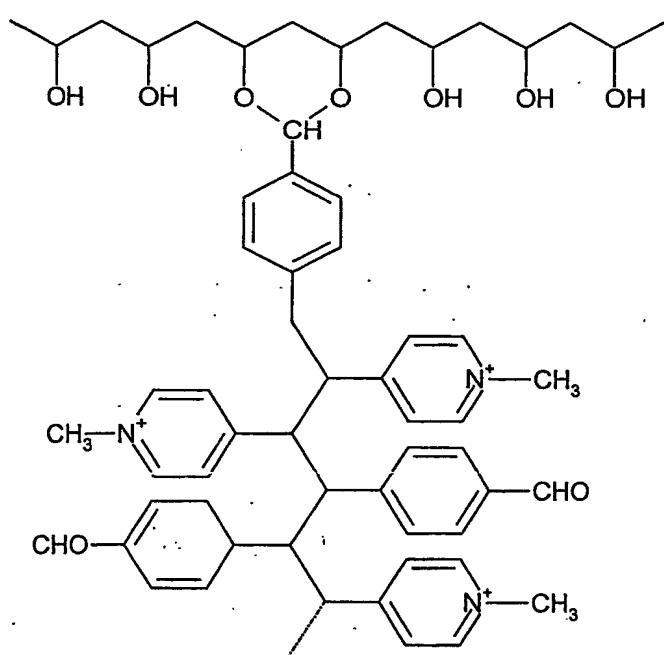
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After addition of the acid, the gelling reaction starts. However, the formulation described takes about 4.5 hours at 25°C to produce a solid gel.

15 The gelling reaction is summarised below:



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 $H^+$ 

A formulation as described in Example 2 has been used to reduce water coning. In use, the formulation is injected to a desired subterranean location. Advantageously, since 5 the formulation includes a substantial amount of water, it has a tendency to be attracted to water. Furthermore, the density of the gel is less than water which means that it has a tendency to migrate to an oil-water interface which may improve its efficacy. Use of the formulation described 10 has been found to reduce water coning significantly and thereby allow increased oil production.

The amounts and/or identity of the components of the formulation of Example 2 may be varied to affect the 15 formation and properties of the gel, as follows:

(a) Butylidene polymer - increasing the concentration of the polymer used tends to shorten the time for the formulation to form a gel. It is preferred to use a 20 butylidene polymer concentration of 10 wt% or less of the amount of polyvinylalcohol in the formulation since higher butylidene polymer concentrations tend to make the gel formed brittle.

(b) Polyvinylalcohol - the concentration affects the time 25 for the formulation to form a gel and the final gel strength. The formulation preferably has a total polyvinylalcohol concentration of 5 wt% or less. If the concentration of polyvinylalcohol in the formulation is too 30 high, the gel tends to form too quickly.

Additionally, the molecular weight of the poly(vinylalcohol) copolymer affects the initial viscosity

of the formulation. For example if only a single type of 88% hydrolysed poly(vinylalcohol) which has a relatively low molecular weight (e.g. about 100,000) is used, then the initial viscosity of the formulation prepared may be 5 relatively low (e.g. about 2cp). However, if a high molecular weight material is used (e.g. of greater than 300,000) the initial viscosity of the formulation will be higher. By selection of one or more polyvinylalcohols of appropriate molecular weight, the viscosity of the 10 formulation may be varied over a wide range.

(c) Diesel fuel - The diesel fuel suitably does not include any additives since such additives can affect gel formation. Consequently, vehicle diesel fuel is preferably 15 not used. The amount of diesel fuel affects the density and strength of the gel. The greater the amount of diesel fuel, the lower the density of the gel which forms and, consequently, the gel has an increased buoyancy which may facilitate its passage to a subterranean oil-water 20 interface. Additionally, increasing the amount of diesel fuel increases the water repellency of the gel which may facilitate its action in reducing coning (and the like). Additionally, increasing the amount of diesel fuel increases the strength of the gel and the gel has a reduced 25 tendency to rupture. It may be that the gel strength is improved by the diesel fuel in a manner akin to the increased strength of rubber when it contains glass beads. As described above, the diesel fuel is emulsified and is present as small droplets in the formulation and in the gel 30 formed therefrom. The droplets may act in a manner similar to the glass beads.

As an alternative to diesel fuel, other organic non-polar materials which suitably are less dense than water may be used such as oils, including vegetable oils and kerosene.

5 The amount of diesel fuel (or an alternative therefor) may represent up to 50wt% of the formulation with the range about 10-20wt% being preferred

(d) Catalyst - This catalyses the reaction of the 10 butylidene polymer and polyvinylalcohol. The amount and identify of the catalyst has consequences for gel strength and the time for the formulation to the gel. In general, increasing the amount of acid tends to increase the rate of formation of the gel; however, the gel may have reduced 15 strength. Mineral acids such as hydrochloric acid may be used and these result in a relatively quick rate of production of gel, compared to PTSA which leads to a slower gelation reaction. In general the lower the pH of the formulation, the quicker the gelation reaction.

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In addition, the formation and properties of the gel may be affected by the temperature and pressure during the gelation reaction. In general, increasing either of these parameters increases the rate of formation of the gel.

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Advantageously, if the formulation and/or the gel formed therefrom are misplaced or otherwise need to be removed, a formulation comprising a periodate (e.g. sodium or potassium periodate) in water, suitably sea water, may be 30 prepared at a concentration up to the saturated solubility limit of the periodate in water. The periodate formulation may then be contacted with the gel-forming formulation described or with the gel formed therefrom. The periodate

causes cleavage of 1,2-diol linkages of the moiety in the gel derived from polyvinylalcohol and consequently the viscosity of the gel forming formulation and/or the gel is reduced, facilitating its removal.

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Attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

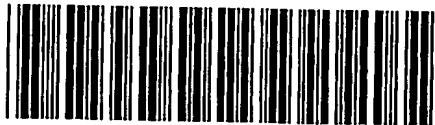
All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

20 Each feature disclosed in this specification (including any accompanying claims, abstract and drawings) may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each 25 feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any 30 novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any

novel one, or any novel combination, of the steps of any method or process so disclosed.

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